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# PHOTOCHEMISTRY AND LIFETIME OF INTERSTELLAR MOLECULES

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PHOTOCHEMISTRY AND LIFETIME OF INTERSTELLAR MOLECULES

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## I. INTRODUCTION

Ammonia was the first polyatomic molecule observed in the interstellar medium and it was detected by means of its emission at 1.25 cm corresponding to the (1,1) inversion transition in the vibrational ground state of the molecule (Cheung, Rank, Townes, Thorton and Welch, 1968). This observation was soon followed by the detection of interstellar water (Cheung, Rank, Townes, Thorton and Welch, 1969) in emission at 1.35 cm and the detection of interstellar formaldehyde ( $\text{H}_2\text{CO}$ ) in absorption at 6.2 cm., (Snyder, Buhl, Zuckerman and Palmer, 1969). More recently identified molecules include CO (Wilson, Jefferts and Penzias, 1970), HCN (Buhl and Snyder, 1970), cyanoacetylene (Turner, 1970), methyl alcohol (Ball, Gottlieb, Lilley and Radford, 1970) and formic acid (Zuckerman, Ball, Gottlieb and Radford, 1970). To this group of molecules detected by radio astronomy we may tentatively add the molecule  $\text{CH}_4$ , since there are indications it may have been detected by absorption in the infrared (Herzberg, 1968).

The detection of polyatomic molecules in the interstellar medium raises questions concerning the mechanism of their formation and their subsequent fate in the interstellar radiation field. While the former problem remains obscure, there is little doubt concerning the latter: once formed, the molecules will be subject to destruction by interstellar photons ( $\lambda > 912 \text{ \AA}$ ). This paper is concerned with a quantitative discussion of the photochemistry and lifetimes of stable interstellar molecules.



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For an interstellar molecule the lifetime against photodecomposition depends upon three factors: the absorption cross section, quantum yield or probability for dissociation following absorption, and the interstellar radiation field. The first two involve the photochemistry of the molecule and are discussed in the following section while the radiation field is discussed in Section III. Section IV presents the method of calculation and results for the lifetimes. The final section discusses briefly various aspects of the results.

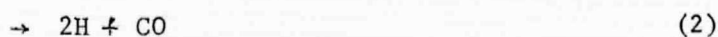
## II. PHOTOCHEMISTRY OF INTERSTELLAR MOLECULES

The absorption cross section and the photochemical decomposition of  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{CH}_4$  have been extensively investigated. The references for the absorption cross sections for each of these molecules is summarized in Table 1. For  $\text{H}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{CO}$  it was necessary to interpolate the data over relatively small wavelength intervals not covered by the references cited. Most of the work on the spectroscopy and photochemistry of  $\text{H}_2\text{CO}$  has been limited to  $\lambda > 2000 \text{ \AA}$ . Few experiments have been performed below  $2000 \text{ \AA}$  where the strong absorption occurs. Indeed, there was not a single quantitative study of the photodecomposition of  $\text{H}_2\text{CO}$  for  $\lambda < 2000 \text{ \AA}$  and the available absorption data (mainly photographic) were either qualitative or covered a very limited wavelength range. The recent determinations in our laboratory of the absorption coefficient for formaldehyde vapor from  $650$  to  $1850 \text{ \AA}$  (Gentieu and Mentall, 1970) and a study of the photochemistry of formaldehyde at  $1470 \text{ \AA}$  and  $1236 \text{ \AA}$  (Glicker and Stief, 1971) are reported in detail elsewhere. With this information on  $\text{H}_2\text{CO}$  and the published data for  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{CH}_4$ , we may now examine the photochemistry of these five molecules as it relates to the interstellar medium. The available data for cyanoacetylene,  $\text{HCN}$ , methyl alcohol and formic acid are insufficient for a quantitative discussion at this time. There is no reason to expect their behavior to differ significantly from the well studied molecules.

### A. Formaldehyde

The average absorption cross section for  $\text{H}_2\text{CO}$  is a thousand times greater in the vacuum ultraviolet region than in the near UV and therefore the photochemistry and lifetime of interstellar formaldehyde will be determined

by photon absorption below 2000 Å. From a study of the photodecomposition of  $\text{H}_2\text{CO}$  at 1470 and 1236 Å (Glicker and Stief, 1971), evidence was obtained for two primary processes:



both of which occurred with a primary quantum yield (molecules decomposed per photon absorbed) of 0.5. No evidence was obtained for any substantial contribution from the process



which, together with process (1), is important for  $\lambda > 2000 \text{ Å}$  (Calvert and Pitts, 1966). Two results are worth noting for our purposes here. One is that the sum of the quantum yields for decomposition by process (1) and (2) is unity, i.e., every photon absorbed leads to decomposition of  $\text{H}_2\text{CO}$ . While this may be safely assumed for a molecule having only continuous absorption (e.g.  $\text{H}_2\text{O}$  or  $\text{CH}_4$ ), it need not be so for molecules with a considerable amount of discrete absorption (e.g.  $\text{CO}$ ,  $\text{H}_2\text{CO}$  and to a lesser extent  $\text{NH}_3$ ). The second point is that the lack of evidence for process (3) at wavelengths below 2000 Å suggests that the formyl radical ( $\text{HCO}$ ) should be a minor product of  $\text{H}_2\text{CO}$  decomposition in the interstellar medium. It may, however, be formed by other means.

#### B. Ammonia

The photodecomposition of ammonia proceeds via the following primary processes (McNesby and Okabe, 1964; Calvert and Pitts, 1966):

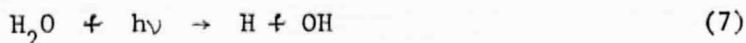


whose relative importance depends on the wavelength of light absorbed. Thus process (4) yielding  $\text{NH}_2 + \text{H}$  is the sole primary process at 2062 Å (Groth, Schurath and Schindler, 1968; Schurath, Tiedman and Schindler, 1969) and 1849 Å (McNesby, Tanaka and Okabe, 1962) while process (5) yielding  $\text{NH} + \text{H}_2$  accounts for about 13% of the primary photodissociation at 1470 Å (Groth, Okabe and Rommel, 1964) and 1236 Å (McNesby, Tanaka and Okabe, 1962), respectively. Presently available data do not allow an estimate to be made of the relative importance of processes (4) and (6) at 1236 Å. Processes (4) and (6) are analogous to processes (3) and (2) in  $\text{H}_2\text{CO}$  photolysis. These results thus suggest that  $\text{NH}_2$  and to a lesser extent  $\text{NH}$  may be present in the interstellar medium as a result of  $\text{NH}_3$  photodecomposition.

The only evidence directly relating to the question of the number of  $\text{NH}_3$  molecules decomposed per photon absorbed comes from the studies at 2062 Å (Schurath, Tiedman and Schindler, 1969). In this study the photolysis of  $\text{NH}_3$  was carried out in the presence of an interceptor or scavenger which transformed the primary fragments ( $\text{H}$  and  $\text{NH}_2$ ) into stable characteristic products. From a quantitative determination of these products, the primary quantum yields of  $\text{H}$  and  $\text{NH}_2$  were estimated to be 0.9 and 0.7 to 0.9 respectively. Thus the primary quantum yield of decomposition is close to unity.

### C. Water

The photodecomposition of water may be considered in terms of two primary processes (McNesby and Okabe, 1964; Calvert and Pitts, 1966):



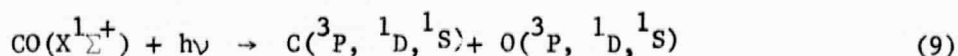
Formation of H and OH is the dominant process at all wavelengths although formation of  $\text{H}_2$  and electronically excited atomic oxygen makes an important contribution ( $\sim 25\%$  of primary process) at  $1236 \text{ \AA}$  (McNesby, Tanaka and Okabe (1962)). At  $1470 \text{ \AA}$ , process (7) accounts for 94% (Stief, 1966) to 100% (Cotton, Masanet and Vermeil, 1966) of the primary process. Thus the principal products of the photodecomposition of water in the interstellar medium are H and OH.

For a molecule such as  $\text{H}_2\text{O}$  with an essentially continuous absorption, all electronic transitions are probably to repulsive states and it may be safely assumed that every photon absorbed leads to dissociation. There is some experimental evidence that this is true for photolysis at  $1470 \text{ \AA}$  (Cotton, Masanet, and Vermeil, 1966).

### D. Carbon Monoxide

The bond energy of CO is 11.1 eV and it is therefore impossible to directly decompose CO with photons of wavelength greater than  $1115 \text{ \AA}$ . Thus only interstellar radiation in the narrow region 912 to  $1115 \text{ \AA}$  will be effective. The photodecomposition of CO has been investigated at wavelengths greater than  $1115 \text{ \AA}$  (Faltings, Groth and Harteck, 1938; Groth, Pessara and Rommel, 1962) and it follows that the reactions of excited molecules are involved. These have little application to the interstellar problem and need not be considered further. Below  $1115 \text{ \AA}$ ,

it is energetically possible to form carbon and oxygen atoms in their  $^3P$ ,  $^1D$  or  $^1S$  states.



The wavelengths below which it is energetically possible to form the indicated carbon and oxygen atoms are summarized below:

C	O	$\Delta H(\text{eV})$	$\lambda(\text{\AA})$
$^3P$	$^3P$	11.11	1115
$^1D$	$^3P$	12.37	1002
$^3P$	$^1D$	13.08	948
$^1S$	$^3P$	13.80	898
$^1D$	$^1D$	14.35	864

Formation of  $C(^1S) + O(^3P)$  and  $C(^1D) + O(^1D)$  are not energetically possible with interstellar photons ( $\lambda > 912 \text{ \AA}$ ) while formation of  $C(^1D) + O(^3P)$  and  $C(^3P) + O(^1D)$  are spin forbidden. The strength of the absorption for much of the region of interest here indicates an allowed transition. Thus the principle products of the photodecomposition of interstellar CO should be carbon and oxygen atoms in their  $^3P$  ground states.



There has been no laboratory work reported on the photolysis of CO below 1115  $\text{\AA}$ . The important question of the fraction of CO molecules decomposed per photon absorbed is impossible to evaluate at present. In contrast to the continuous nature of the absorption spectra for the other molecule considered here (especially  $\text{CH}_4$ ,  $\text{H}_2\text{O}$  and to a lesser extent  $\text{NH}_3$  and  $\text{H}_2\text{CO}$ ), CO exhibits very strong discrete absorption with what may



be a relatively weak underlying continuous absorption. Thus photon absorption may lead to appreciable formation of long-lived excited states and the primary quantum yield of CO decomposition could be considerably less than unity.

#### E. Methane

The photochemistry of methane has been discussed in terms of the primary processes (McNesby and Okabe, 1964; Calvert and Pitts, 1966):



The dominant process at all wavelengths studied is process (11) yielding molecular hydrogen and the methylene radical (Laufer and McNesby, 1968; Gordon and Ausloos, 1967). The relative quantum yield of the minor process

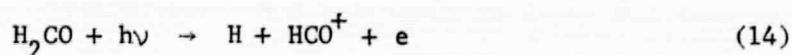


increases about threefold when the wavelength is reduced from 1236 Å to 1048-1067 Å (Gordon and Ausloos, 1967). These results therefore suggest that if  $\text{CH}_4$  is indeed present in the interstellar medium, there should also be present the undetected radicals  $\text{CH}_2$  and  $\text{CH}_3$ .

Methane has a continuous absorption spectrum in the vacuum UV and it may be assumed that every photon absorbed leads to dissociation. This is confirmed by the careful quantum yield measurement of Laufer and McNesby (1968) which, combined with the data of Gordon and Ausloos (1967) on the relative importance of processes leading to  $\text{CH}$ ,  $\text{CH}_3$  and  $\text{H}_2$ , demonstrate that the sum of the quantum yields for the known primary processes is 0.9 for photolysis at 1236 Å.

#### f. Photoionization

In addition to the photodecomposition processes discussed above, interstellar molecules may be ionized as a result of interaction with the interstellar radiation field. Table 2 summarizes the available data on the ionization potential of these molecules and gives the wavelength corresponding to the ionization threshold. It is evident that for  $\lambda > 912 \text{ \AA}$ , the formation of parent molecule ions is energetically possible for all the molecules considered here with the exception of CO and probably HCN. Ionization will in general be somewhat less important than fragmentation since the average ionization efficiencies for  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{CH}_4$  from their ionization thresholds to  $912 \text{ \AA}$  are approximately 40% (Watanabe and Sood, 1965) 33% and 10% respectively (Metzger and Cook, 1964). Ionization will be even less important in clouds due to attenuation of the short-wavelength. Simultaneous fragmentation and ionization upon single photon absorption is not energetically possible at  $\lambda > 912 \text{ \AA}$  with the possible exception of the process



which has a threshold at 13.4 eV (925Å).



### III. THE INTERSTELLAR RADIATION FIELD

The interstellar radiation field which a molecule sees will vary considerably depending primarily upon the degree of obscuration in the vicinity of the molecule. As we are concerned with continuous rather than line absorption, only the grains will contribute. The effect of interstellar extinction and its spatial fluctuations on interstellar chemistry must be examined.

In the so-called clear regions of the Milky Way the extinction in the visible is a few tenths magnitude per kiloparsec (Bok, 1936). We refer to these regions as unobscured. Several calculations of the interstellar radiation field appropriate to the unobscured regions have been carried out. These are in general agreement except near Lyman- $\alpha$  for which Lambrecht and Zimmerman (1956) have a peak several times greater than the rather flat distribution of other investigators. Their result which approximately doubles the ultraviolet flux does not significantly increase the uncertainty of the calculation. We adopt here the results of Habing (1968) who obtains an ultraviolet energy density  $U_\lambda$  between 30 and  $50 \times 10^{-18}$  ergs cm $^{-3}$  Å $^{-1}$  between 1000 and 2200 Å. Lambrecht and Zimmerman's (1956) results for wavelength to 3646 Å are sufficiently consistent with this value that we have adopted a constant  $U_\lambda = 40 \times 10^{-18}$  ergs cm $^{-3}$  Å $^{-1}$  for  $\lambda > 912$  Å. This calculated density agrees very well with the measured flux of Lillie (1968) for the same wavelength range. The uncertainty of the calculations and the small effect on the lifetimes do not warrant the additional work of allowing for any wavelength dependence.

Radio observations of interstellar molecules permits their spatial distribution to be determined and indicate an association with obscured regions. Consequently, it is necessary to determine the

radiation field in obscuring clouds. This has been done by combining the adopted constant flux with an interstellar extinction curve covering the visible and ultraviolet regions. For the visible we used Johnson's (1965) curve for the Perseus region and for the ultraviolet, Stecher's (1969) curve determined from rocket observations of Persei. These results are in general agreement with the satellite observations of Code (1969). In both wavelength intervals regional variations in the extinction curve are found. Errors are introduced by using data from only one region for the entire Milky Way. However, the Perseus curve appears to be applicable within an acceptable uncertainty to several other areas. An uncertainty difficult to evaluate arises from the assumption that grains in the low density, relatively unobscured regions have the same optical properties as in much more highly obscured, denser clouds where the molecules are found. Although these factors in the analysis should be kept in mind, we will go ahead on the hypothesis that the final results are qualitatively correct and that the uncertainty is not large enough to affect conclusions regarding the stability and origin of molecules. It will be seen from the results that this hypothesis is justified.

Stecher's and Johnson's curve overlaps at the U point. From Table 5 of Johnson,  $A_U = 4.7$  for  $B-V = 1$ , to which value the ultraviolet curve is normalized. Figure 1 presents the Perseus extinction curve on an absolute basis. This was obtained by redrawing Stecher's curve with the ordinate displaced to make  $A_U = 4.7$ , extrapolating the curve to  $1/\lambda = 10 \mu^{-1}$  and using Johnson's curve for the long wavelength end.

We next determined the radiation field which has penetrated zones of increasing optical thickness measured by the visible extinction,  $A_V$ . Steps

of 1.0 in  $A_V$  were chosen and the extinction determined at a series of wavelengths to 900 Å by multiplying the normalized set by  $A_V/3$  ( $A_V = 3$  on the normalized curve of Figure 1). These magnitudes were converted into transmissivities. Figure 2 is a plot of transmissivity as a function of wavelength for various optical depths in a cloud. These transmissivities may be multiplied by the adopted uniform interstellar radiation field to obtain the radiation field as a function of cloud depth.

#### IV. LIFETIME OF INTERSTELLAR MOLECULES

The probability  $P$  that a molecule is decomposed by light in the interstellar medium is given by:

$$P = \int N_{\lambda} \phi_{\lambda} d\lambda \quad (15)$$

where  $N_{\lambda}$  = number of photons absorbed by the molecule in the interval  $d\lambda$  and the limits of integration are from 912 Å to the photodissociation threshold.

$\phi_{\lambda}$  = the primary quantum yield of decomposition (i.e the probability of dissociation per absorbed photon).

In terms of the energy density  $U_{\lambda}$ , equation 15 becomes

$$P = 1/h \int U_{\lambda} \sigma_{\lambda} \phi_{\lambda} \lambda d\lambda \quad (16)$$

where  $h$  = Planck's constant. The derivation of equation 16 is given in the Appendix. The lifetime of the molecule against photodecomposition is simply the reciprocal of the dissociation probability  $P$ .

$P$  is determined by integration of the product over all wavelengths from 912 Å to the photodissociation threshold of the molecule. However, as discussed in the last section, it is likely that  $U_{\lambda}$  does not vary by more than a factor of about two over the wavelength interval 1000 to 3600 Å and, with the exception of cloud areas, also does not vary by more than a small factor throughout interstellar space. Therefore in interstellar space free of obscuring clouds the dissociation probability can be written

$$P = U < \sigma \lambda > \phi / h \quad (17)$$

where  $U$  is the integrated energy density.

For all molecules discussed in Section II except carbon monoxide we put  $\Phi = 1$ . Carbon monoxide lifetimes were calculating using both  $\Phi = 1$  and 0.1.

It is obvious that lifetimes will be orders of magnitude longer in clouds where there is high obscuration of interstellar radiation. In order to examine the effect of increasing depth of the cloud, we have calculated the lifetimes of  $H_2CO$ ,  $H_2O$ ,  $NH_3$ ,  $CO$  and  $CH_4$  as a function of increasing optical thickness. The latter is measured in terms of the extinction in the visual,  $A_v$ , as discussed in Part III and shown in Fig. 2 as a plot of transmissivity  $T_\lambda$  vs  $\lambda$  for steps of 1.0 in  $A_v$ .

The dissociation probability for an obscured region is given by

$$P = \frac{U\Phi}{h} \int T_\lambda \sigma_\lambda \lambda d\lambda = U \langle T\sigma\lambda \rangle \Phi/h \quad (18)$$

The procedure was to plot the product  $T\sigma\lambda$  vs  $\lambda$  and obtain  $\langle T\sigma\lambda \rangle$  from the area under the curve. In practice, both of these were done numerically on a computer with areas determined by the spline interpolation method (Thompson, 1970). Comparison with values determined by hand plotting and area measurements with a planimeter showed agreement to within 10% for lifetimes in unobscured regions, indicating that the interpolation method is satisfactory even for molecules with rapidly varying cross sections.

Figure 3 shows lifetimes against photodecomposition in unobscured regions (represented by  $A_v = 0$ ) and in regions with increasing degrees of obscuration ( $A_v = 1, 2, 3$  and 4 magnitudes).

## V. DISCUSSION

The results in Figure 3 indicates that in clear interstellar regions all molecules except carbon monoxide have comparable lifetimes of less than 100 years. These are all extremely short on the galactic time scale. Thus, the molecules water, ammonia, methane, and formaldehyde can exist only in dense clouds which protect them from the full interstellar radiation field. This is consistent with observations of ammonia (Cheung et al. 1969b) and formaldehyde (Zuckerman, et al. 1970). Further, these molecules can never have been exposed to the unobscured radiation from the time of formation until protected in clouds. This requirement imposes a severe restriction on possible mechanisms of formation. It implies that polyatomic molecules were formed or released in the gas phase in the clouds where they now occur.

The lifetime obtained here for  $\text{NH}_3$  ( $\tau = 40$  years) is less than that estimated by Cheung et al (1968), ( $\tau = 100$  years). The difference is due to their use of a cross section ( $3.7 \times 10^{-18} \text{ cm}^2$ ) given by Potter and DelDuca (1964) for the region down to  $1216 \text{ \AA}$ . The interstellar radiation field extends down to  $912 \text{ \AA}$  and the average absorption cross section for  $\text{NH}_3$  in the region  $912\text{-}1050 \text{ \AA}$  is three times larger than it is in the region  $1050\text{-}2200 \text{ \AA}$ . This results in a larger dissociation probability  $P$  and hence a shorter lifetime.

The carbon monoxide lifetime is 2 to 20 times longer than that for the other molecules considered here, depending upon the value of



the quantum yield. The CO molecules therefore require considerably less protection than formaldehyde and the other interstellar molecules. This property can readily explain the observation (Wilson, Jefferts and Penzias, 1970) that the size of the carbon monoxide cloud is at least an order of magnitude larger than that of a typical formaldehyde cloud. The smaller quantum yield for carbon monoxide leads to a lifetime of  $10^3$  years which is comparable to that of molecular hydrogen (Stecher and Williams, 1967), and the OH and CH radicals (Hesser and Lutz, 1970).

Stecher and Williams (1966) give a rough estimate of  $10^6$  years for the lifetime of CO in a  $10,000^\circ\text{K}$  radiation field with a dilution factor of  $3 \times 10^{-15}$ . We have corrected this to the uniform Habing field and obtain  $10^4$  years. For this to be in agreement with the results of Fig. 3, the quantum yield  $\phi$  would have to be  $10^{-2}$ .

Figure 3 shows, as expected, that the lifetimes of molecules in clouds with a few magnitudes extinction become the order of  $10^6$  years. Contrary to the lifetime of less than one hundred years estimated in the cloud-free regions, lifetimes in clouds of moderate opacity are sufficiently long for the molecules to be more than transient residents of interstellar space. It is also worth noting that the order of lifetimes in the denser clouds is  $\text{CH}_4 > \text{H}_2\text{O} \approx \text{NH}_3 > \text{H}_2\text{CO}$ . This is expected since the long wavelength cut-off of absorption increases in this same order, viz: 1600 Å, 1850 Å, 2200 Å and 3800 Å respectively for  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{H}_2\text{CO}$ , and the degree of protection is reduced.

In addition to photodissociation and any photoionization that occurs, molecules can also be destroyed by interaction with high energy radiation (X and  $\gamma$ -rays) and energetic particles. These processes are

much less effective than destruction by ultraviolet radiation. However, when the ultraviolet is highly attenuated in clouds, the energetic radiation and particles will persist and become relatively more important. The ultimate lifetimes in clouds may depend upon these processes and may be shorter than those shown in Figure 3. These processes require further study.

#### APPENDIX

The absorption coefficient measured in the laboratory is an average over all orientations of the molecule in a nearly uni-directional radiation field. This process yields a spherically-symmetric average cross-section.

The energy falling per-unit time on a sphere of cross section area  $\sigma$  within a cone  $d\Omega$  from a given direction is

$$dE = I\sigma d\Omega. \quad (A1)$$

Integration over all solid angles yields the total energy falling on the sphere:

$$E = 4\pi I\sigma \quad (A2)$$

For an isotropic radiation field of energy density  $U$ , the intensity is given by the relation (Chandrasekhar, 1939)

$$I = \frac{c}{4\pi} U \quad (A3)$$

Upon substituting this into equation A2 we obtain

$$E = U c \sigma \quad (A4)$$



To convert into number of photons, we divide by  $hc/\lambda$  giving

$$N_{\lambda} = \frac{U\sigma\lambda}{h} \cdot \quad (A5)$$

When this is inserted into equation 15, equation 16 results. Because of the symmetry of the cross section, the right hand side of equation A4 is not divided by 4 as is the case with the flux in an isotropic radiation field.

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TABLE I  
REFERENCES FOR ABSORPTION CROSS SECTIONS  $\sigma$  OF INTERSTELLAR MOLECULE

Molecule	Wavelength Interval	Reference
$\text{H}_2\text{CO}$	912 - 1850 Å	Gentieu and Mentall (1970)
	2000 - 3600 Å	Calvert and Pitts (1966)
$\text{NH}_3$	912 - 1050 Å	Watanabe and Sood (1965)
	1050 - 2200 Å	Samson and Myer (1969)
$\text{H}_2\text{O}$	912 - 988 Å	Metzger and Cook (1964)
	1050 - 1850 Å	Samson and Myer (1969)
$\text{CH}_4$	912 - 1000 Å	Metzger and Cook (1964)
	1150 - 1600 Å	Samson and Myer (1969)
CO	912 - 976 Å	Cook, Metzger and Ogawa (1965)
	1050 - 1115 Å	Samson and Myer (1969)

TABLE 2

Ionization Potentials and Threshold Wavelengths for Ionization of Interstellar Molecules

Molecule	IP (eV)	$\lambda$ (Å)	Reference
NH <sub>3</sub>	10.2	1215	Watanabe (1957)
CH	10.6	1170	Herzberg and Johns (1969)
H <sub>2</sub> CO	10.9	1137	Watanabe (1957)
CH <sub>3</sub> OH	10.9	1137	Watanabe (1957)
HCOOH	11.1	1117	Watanabe (1957)
H-C≡C-CN	11.6	1069	Diebler, Reese and Franklin (1961).
H <sub>2</sub> O	12.6	984	Watanabe (1957)
CH <sub>4</sub>	13.0	954	Watanabe (1957)
OH	13.1	946	Foner and Hudson (1958)
HCN	13.6	912	Diebler and Liston (1968)
H	13.6	912	
CO	14.0	886	Watanabe (1957)
CN	14.2	873	Diebler and Liston (1967)

# CAPTIONS FOR FIGURES

Figure 1. Extinction curve for the perseus region. Dotted portion is an extrapolation.

Figure 2. Transmissivity in cloud as a function of wavelength.  
 $A_v$  is the cloud extinction in magnitudes at 5500 Å.

Figure 3. Lifetime of Interstellar Molecules in clouds.

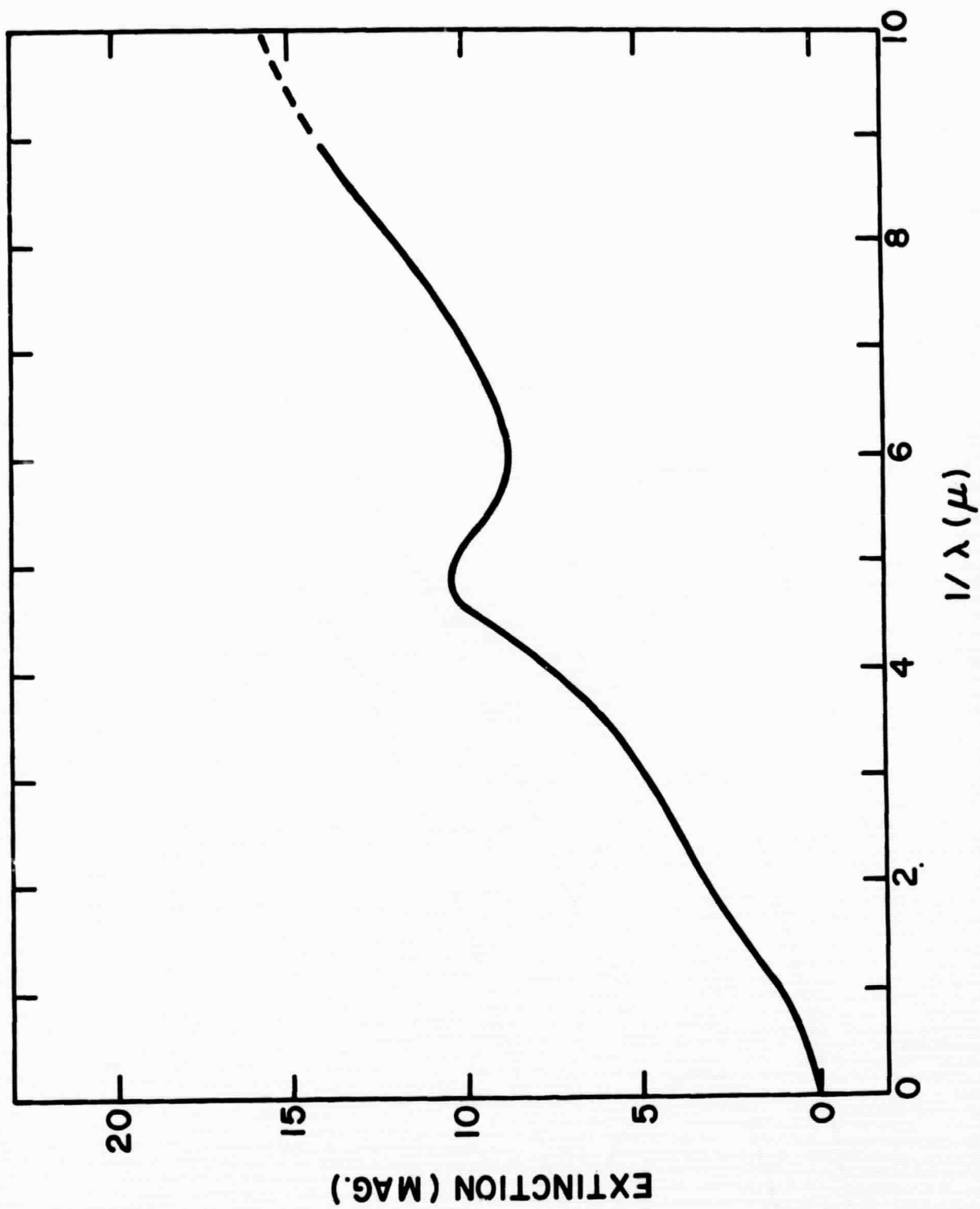


Figure 1



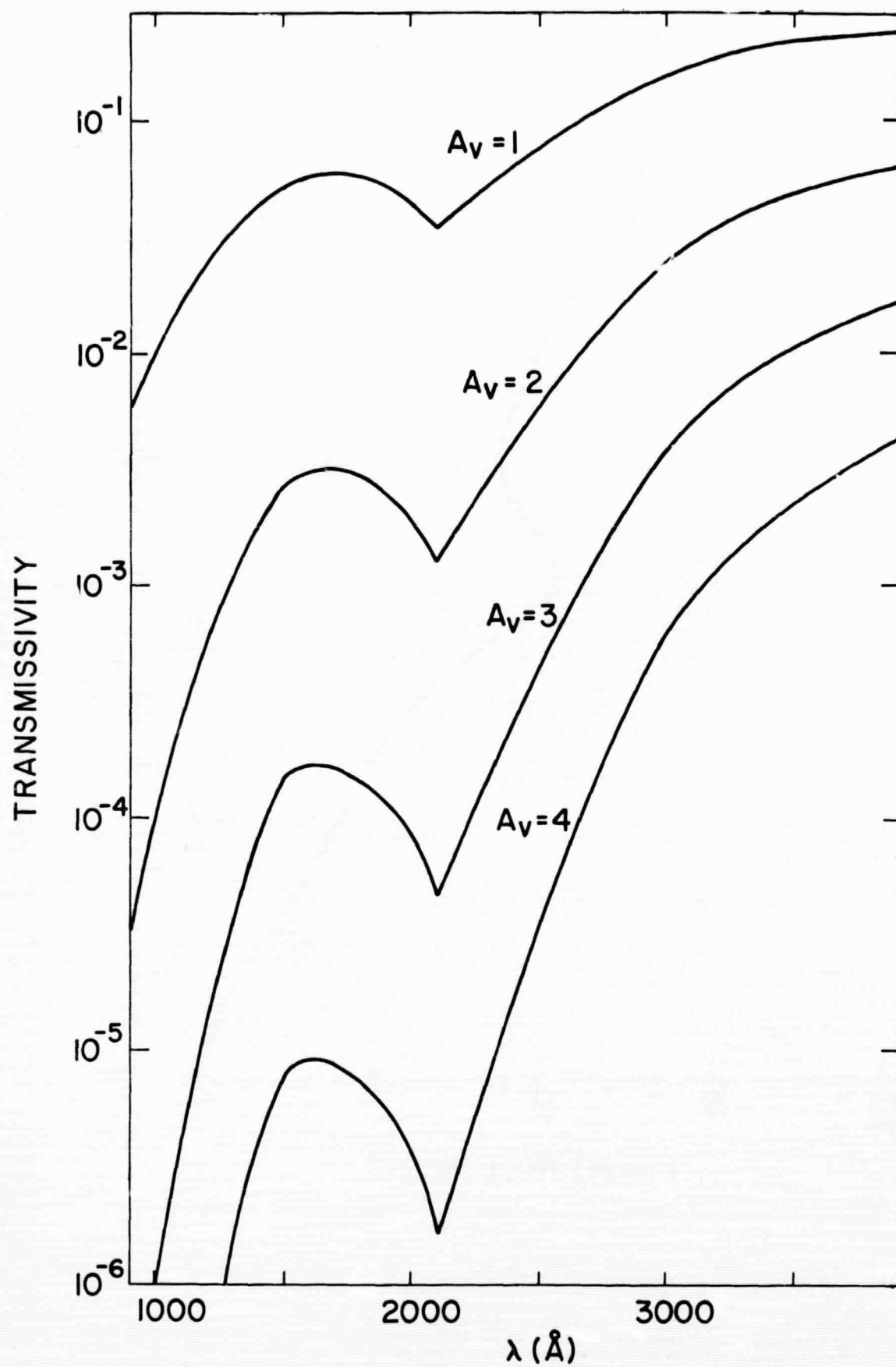


Figure 2

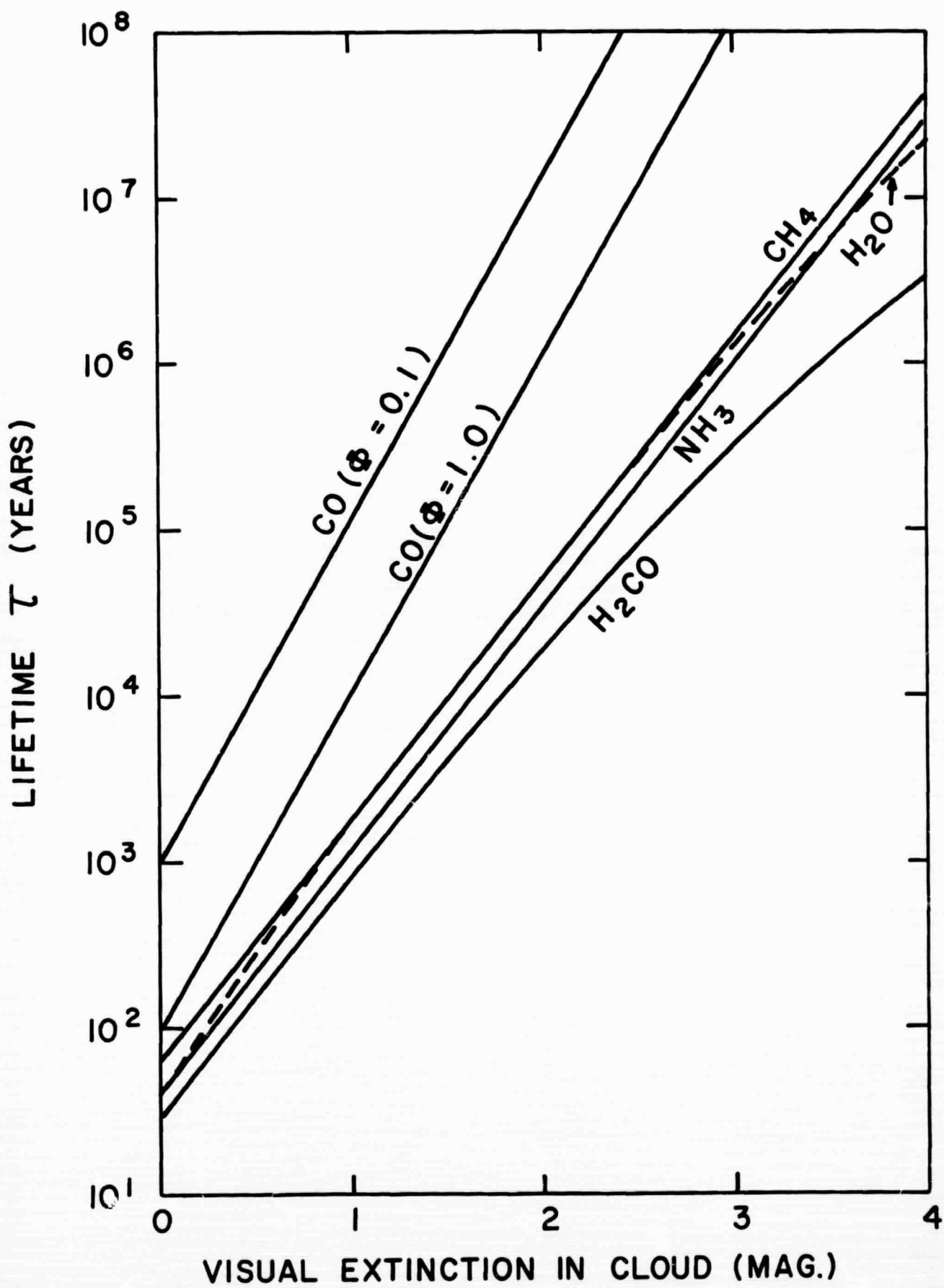


Figure 3

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PHOTOCHEMISTRY AND LIFETIME OF INTERSTELLAR MOLECULES

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## I. INTRODUCTION

Ammonia was the first polyatomic molecule observed in the interstellar medium and it was detected by means of its emission at 1.25 cm corresponding to the (1,1) inversion transition in the vibrational ground state of the molecule (Cheung, Rank, Townes, Thorton and Welch, 1968). This observation was soon followed by the detection of interstellar water (Cheung, Rank, Townes, Thorton and Welch, 1969) in emission at 1.35 cm and the detection of interstellar formaldehyde ( $\text{H}_2\text{CO}$ ) in absorption at 6.2 cm., (Snyder, Buhl, Zuckerman and Palmer, 1969). More recently identified molecules include CO (Wilson, Jefferts and Penzias, 1970), HCN (Buhl and Snyder, 1970), cyanoacetylene (Turner, 1970), methyl alcohol (Ball, Gottlieb, Lilley and Radford, 1970) and formic acid (Zuckerman, Ball, Gottlieb and Radford, 1970). To this group of molecules detected by radio astronomy we may tentatively add the molecule  $\text{CH}_4$ , since there are indications it may have been detected by absorption in the infrared (Herzberg, 1968).

The detection of polyatomic molecules in the interstellar medium raises questions concerning the mechanism of their formation and their subsequent fate in the interstellar radiation field. While the former problem remains obscure, there is little doubt concerning the latter: once formed, the molecules will be subject to destruction by interstellar photons ( $\lambda > 912 \text{ \AA}$ ). This paper is concerned with a quantitative discussion of the photochemistry and lifetimes of stable interstellar molecules.

7

For an interstellar molecule the lifetime against photodecomposition depends upon three factors: the absorption cross section, quantum yield or probability for dissociation following absorption, and the interstellar radiation field. The first two involve the photochemistry of the molecule and are discussed in the following section while the radiation field is discussed in Section III. Section IV presents the method of calculation and results for the lifetimes. The final section discusses briefly various aspects of the results.



## II. PHOTOCHEMISTRY OF INTERSTELLAR MOLECULES

The absorption cross section and the photochemical decomposition of  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{CH}_4$  have been extensively investigated. The references for the absorption cross sections for each of these molecules is summarized in Table 1. For  $\text{H}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{CO}$  it was necessary to interpolate the data over relatively small wavelength intervals not covered by the references cited. Most of the work on the spectroscopy and photochemistry of  $\text{H}_2\text{CO}$  has been limited to  $\lambda > 2000 \text{ \AA}$ . Few experiments have been performed below  $2000 \text{ \AA}$  where the strong absorption occurs. Indeed, there was not a single quantitative study of the photodecomposition of  $\text{H}_2\text{CO}$  for  $\lambda < 2000 \text{ \AA}$  and the available absorption data (mainly photographic) were either qualitative or covered a very limited wavelength range. The recent determinations in our laboratory of the absorption coefficient for formaldehyde vapor from  $650$  to  $1850 \text{ \AA}$  (Gentieu and Mentall, 1970) and a study of the photochemistry of formaldehyde at  $1470 \text{ \AA}$  and  $1236 \text{ \AA}$  (Glicker and Stief, 1971) are reported in detail elsewhere. With this information on  $\text{H}_2\text{CO}$  and the published data for  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{CH}_4$ , we may now examine the photochemistry of these five molecules as it relates to the interstellar medium. The available data for cyanoacetylene,  $\text{HCN}$ , methyl alcohol and formic acid are insufficient for a quantitative discussion at this time. There is no reason to expect their behavior to differ significantly from the well studied molecules.

### A. Formaldehyde

The average absorption cross section for  $\text{H}_2\text{CO}$  is a thousand times greater in the vacuum ultraviolet region than in the near UV and therefore the photochemistry and lifetime of interstellar formaldehyde will be determined

by photon absorption below 2000 Å. From a study of the photodecomposition of H<sub>2</sub>CO at 1470 and 1236 Å (Glicker and Stief, 1971), evidence was obtained for two primary processes:



both of which occurred with a primary quantum yield (molecules decomposed per photon absorbed) of 0.5. No evidence was obtained for any substantial contribution from the process



which, together with process (1), is important for  $\lambda > 2000$  Å (Calvert and Pitts, 1966). Two results are worth noting for our purposes here. One is that the sum of the quantum yields for decomposition by process (1) and (2) is unity, i.e., every photon absorbed leads to decomposition of H<sub>2</sub>CO. While this may be safely assumed for a molecule having only continuous absorption (e.g. H<sub>2</sub>O or CH<sub>4</sub>), it need not be so for molecules with a considerable amount of discrete absorption (e.g. CO, H<sub>2</sub>CO and to a lesser extent NH<sub>3</sub>). The second point is that the lack of evidence for process (3) at wavelengths below 2000 Å suggests that the formyl radical (HCO) should be a minor product of H<sub>2</sub>CO decomposition in the interstellar medium. It may, however, be formed by other means.

#### B. Ammonia

The photodecomposition of ammonia proceeds via the following primary processes (McNesby and Okabe, 1964; Calvert and Pitts, 1966):





whose relative importance depends on the wavelength of light absorbed. Thus process (4) yielding  $\text{NH}_2 + \text{H}$  is the sole primary process at 2062 Å (Groth, Schurath and Schindler, 1968; Schurath, Tiedman and Schindler, 1969) and 1849 Å (McNesby, Tanaka and Okabe, 1962) while process (5) yielding  $\text{NH} + \text{H}_2$  accounts for about 13% of the primary photodissociation at 1470 Å (Groth, Okabe and Rommel, 1964) and 1236 Å (McNesby, Tanaka and Okabe, 1962), respectively. Presently available data do not allow an estimate to be made of the relative importance of processes (4) and (6) at 1236 Å. Processes (4) and (6) are analogous to processes (3) and (2) in  $\text{H}_2\text{CO}$  photolysis. These results thus suggest that  $\text{NH}_2$  and to a lesser extent  $\text{NH}$  may be present in the interstellar medium as a result of  $\text{NH}_3$  photodecomposition.

The only evidence directly relating to the question of the number of  $\text{NH}_3$  molecules decomposed per photon absorbed comes from the studies at 2062 Å (Schurath, Tiedman and Schindler, 1969). In this study the photolysis of  $\text{NH}_3$  was carried out in the presence of an interceptor or scavenger which transformed the primary fragments ( $\text{H}$  and  $\text{NH}_2$ ) into stable characteristic products. From a quantitative determination of these products, the primary quantum yields of  $\text{H}$  and  $\text{NH}_2$  were estimated to be 0.9 and 0.7 to 0.9 respectively. Thus the primary quantum yield of decomposition is close to unity.

### C. Water

The photodecomposition of water may be considered in terms of two primary processes (McNesby and Okabe, 1964; Calvert and Pitts, 1966):



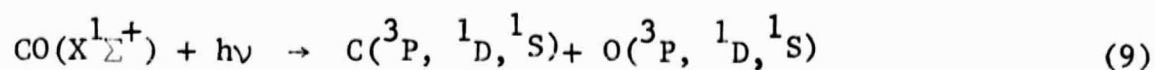
Formation of H and OH is the dominant process at all wavelengths although formation of  $\text{H}_2$  and electronically excited atomic oxygen makes an important contribution ( $\sim 25\%$  of primary process) at  $1236 \text{ \AA}$  (McNesby, Tanaka and Okabe (1962)). At  $1470 \text{ \AA}$ , process (7) accounts for 94% (Stief, 1966) to 100% (Cotton, Masanet and Vermeil, 1966) of the primary process. Thus the principal products of the photodecomposition of water in the interstellar medium are H and OH.

For a molecule such as  $\text{H}_2\text{O}$  with an essentially continuous absorption, all electronic transitions are probably to repulsive states and it may be safely assumed that every photon absorbed leads to dissociation. There is some experimental evidence that this is true for photolysis at  $1470 \text{ \AA}$  (Cotton, Masanet, and Vermeil, 1966).

### D. Carbon Monoxide

The bond energy of CO is 11.1 eV and it is therefore impossible to directly decompose CO with photons of wavelength greater than  $1115 \text{ \AA}$ . Thus only interstellar radiation in the narrow region 912 to  $1115 \text{ \AA}$  will be effective. The photodecomposition of CO has been investigated at wavelengths greater than  $1115 \text{ \AA}$  (Faltings, Groth and Harteck, 1938; Groth, Pessara and Rommel, 1962) and it follows that the reactions of excited molecules are involved. These have little application to the interstellar problem and need not be considered further. Below  $1115 \text{ \AA}$ ,

it is energetically possible to form carbon and oxygen atoms in their  $^3P$ ,  $^1D$  or  $^1S$  states.



The wavelengths below which it is energetically possible to form the indicated carbon and oxygen atoms are summarized below:

C	O	$\Delta H(\text{eV})$	$\lambda(\text{\AA})$
$^3P$	$^3P$	11.11	1115
$^1D$	$^3P$	12.37	1002
$^3P$	$^1D$	13.08	948
$^1S$	$^3P$	13.80	898
$^1D$	$^1D$	14.35	864

Formation of  $C(^1S) + O(^3P)$  and  $C(^1D) + O(^1D)$  are not energetically possible with interstellar photons ( $\lambda > 912 \text{ \AA}$ ) while formation of  $C(^1D) + O(^3P)$  and  $C(^3P) + O(^1D)$  are spin forbidden. The strength of the absorption for much of the region of interest here indicates an allowed transition. Thus the principle products of the photodecomposition of interstellar CO should be carbon and oxygen atoms in their  $^3P$  ground states.



There has been no laboratory work reported on the photolysis of CO below 1115  $\text{\AA}$ . The important question of the fraction of CO molecules decomposed per photon absorbed is impossible to evaluate at present. In contrast to the continuous nature of the absorption spectra for the other molecule considered here (especially  $\text{CH}_4$ ,  $\text{H}_2\text{O}$  and to a lesser extent  $\text{NH}_3$  and  $\text{H}_2\text{CO}$ ), CO exhibits very strong discrete absorption with what may

be a relatively weak underlying continuous absorption. Thus photon absorption may lead to appreciable formation of long-lived excited states and the primary quantum yield of CO decomposition could be considerably less than unity.

#### E. Methane

The photochemistry of methane has been discussed in terms of the primary processes (McNesby and Okabe, 1964; Calvert and Pitts, 1966):



The dominant process at all wavelengths studied is process (11) yielding molecular hydrogen and the methylene radical (Laufer and McNesby, 1968; Gordon and Ausloos, 1967). The relative quantum yield of the minor process



increases about threefold when the wavelength is reduced from 1236 Å to 1048-1067 Å (Gordon and Ausloos, 1967). These results therefore suggest that if CH<sub>4</sub> is indeed present in the interstellar medium, there should also be present the undetected radicals CH<sub>2</sub> and CH<sub>3</sub>.

Methane has a continuous absorption spectrum in the vacuum UV and it may be assumed that every photon absorbed leads to dissociation. This is confirmed by the careful quantum yield measurement of Laufer and McNesby (1968) which, combined with the data of Gordon and Ausloos (1967) on the relative importance of processes leading to CH, CH<sub>3</sub> and H<sub>2</sub>, demonstrate that the sum of the quantum yields for the known primary processes is 0.9 for photolysis at 1236 Å.

#### f. Photoionization

In addition to the photodecomposition processes discussed above, interstellar molecules may be ionized as a result of interaction with the interstellar radiation field. Table 2 summarizes the available data on the ionization potential of these molecules and gives the wavelength corresponding to the ionization threshold. It is evident that for  $\lambda > 912 \text{ \AA}$ , the formation of parent molecule ions is energetically possible for all the molecules considered here with the exception of CO and probably HCN. Ionization will in general be somewhat less important than fragmentation since the average ionization efficiencies for  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  and  $\text{CH}_4$  from their ionization thresholds to  $912 \text{ \AA}$  are approximately 40% (Watanabe and Sood, 1965) 33% and 10% respectively (Metzger and Cook, 1964). Ionization will be even less important in clouds due to attenuation of the short-wavelength. Simultaneous fragmentation and ionization upon single photon absorption is not energetically possible at  $\lambda > 912 \text{ \AA}$  with the possible exception of the process



which has a threshold at 13.4 eV (925Å).

much less effective than destruction by ultraviolet radiation. However, when the ultraviolet is highly attenuated in clouds, the energetic radiation and particles will persist and become relatively more important. The ultimate lifetimes in clouds may depend upon these processes and may be shorter than those shown in Figure 3. These processes require further study.

#### APPENDIX

The absorption coefficient measured in the laboratory is an average over all orientations of the molecule in a nearly uni-directional radiation field. This process yields a spherically-symmetric average cross-section.

The energy falling per-unit time on a sphere of cross section area  $\sigma$  within a cone  $d\Omega$  from a given direction is

$$dE = I\sigma d\Omega. \quad (A1)$$

Integration over all solid angles yields the total energy falling on the sphere:

$$E = 4\pi I\sigma \quad (A2)$$

For an isotropic radiation field of energy density  $U$ , the intensity is given by the relation (Chandrasekhar, 1939)

$$I = \frac{C}{4\pi} U \quad (A3)$$

Upon substituting this into equation A2 we obtain

$$E = U\sigma C \quad (A4)$$

To convert into number of photons, we divide by  $hc/\lambda$  giving

$$N_{\lambda} = \frac{U\sigma\lambda}{h} \cdot \quad (A5)$$

When this is inserted into equation 15, equation 16 results. Because of the symmetry of the cross section, the right hand side of equation A4 is not divided by 4 as is the case with the flux in an isotropic radiation field.

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